

86-078194/12 A82 G02 (A14) KAPA 17.07.84
 KANSAI PAINT KK *J6 1026-608-A
 17.07.84-JP-146994 (05.02.86) C08f-220/28 C08f-226/06
 Aq. pigment dispersion for paints - using dispersant obtd. by
 copolymerising modified (meth)acrylate with unsatd. monomers and
 quat. ammonium gp.-contg. (meth)acrylate
 C86-033338

In an aq. dispersion comprising (a) a pigment, (b) a disper-
 sing material and (c) an aq. medium, the dispersing material
 comprises a water soluble polymer obtd. by polymerising

(1) 1-98 pts. wt. of (meth)acrylate modified with (i) an
 aliphatic acid, (ii) a lactone or condensate of oxyacid or (iii)
 a mono- or poly-alkylene glycol or its monoether deriv.;

(2) 2-97 pts. wt. of an α,β -ethylenically unsatd. cpd.
 having an N atom.;

(3) 0.5-30 pts. wt. of (meth)acrylate having a quarter-
 nary ammonium gp. and

(4) 0-91 pts. wt. of an α,β -ethylenically unsatd. mono-
 mer.

ADVANTAGE/USE

The dispersion is added to aq. paints, e.g. emulsion,
 and coloured paints. The paint has improved dispersion stab-
 ility and film performance.

A(4-D1, 4-D9, 4-F6E7, 7-B2, 12-B1A, 12-B1E) G(2-A2C, 2-
 A2C3, 2-A3)

The dispersion has improved storage stability and pig-
 ment dispersion property on using a small amt. of the dis-
 persing material.

MATERIAL AND AMOUNTS

The aliphatic acid (i) is obtd. from natural oil, fat, ali-
 phatic acid or petroleum and is pref. e.g. 4-24 C satd. ali-
 phatic acid.

The (meth)acrylate (1) is e.g. (meth)acrylate having
 epoxy or hydroxy gp..

1 mol. of the acid (i) and 0.7-1.5 mol of the acrylate are
 reacted at 60-220°C for 0.5-40 hrs..

100 pts. wt. of the pigment (a) and 1-540 pts. wt. of the
 dispersing material (b) are mixed.

EXAMPLE

236 pts. wt. of aliphatic acid obtd. from safflower oil,
 119 pts. wt. of glycidyl methacrylate, 0.4 pt. wt. of hydro-
 quinone and 0.2 pt. wt. of tetraethylammonium m-bromide are
 mixed and agitated at 140-150°C for 4 hrs.. The aliphatic
 acid modified acrylate is obtd..

350 pts. wt. of n-butyl cellulose is charged in a reactor

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and maintained at 120°C. 118 pts. wt. of the modified acryl-
 ate, 126 pts. wt. of N-vinyl pyrrolidone, 6 pts. wt. of an aq.
 soln. contg. methacryloxyethyltrimethylammonium-chloride
 (50%) and 17.5 pts. wt. of azobisisobutyronitrile (AZBN) are
 added for 2 hrs..

The mixt. is agitated for 1 hr.. 2.5 pts. wt. of AZBN is
 added and agitated for 2 hrs.. 2.5 pts. wt. of AZBN is again
 added and agitated at 80°C for 2 hrs to obtain the dispersing
 material.

The soln. and water are mixed (40% solids content), and
 an aq. dispersion (A) is obtd.. 8.3 pts. wt. of dispersion
 (A) and 200 pts. wt. of TiO_2 are mixed and agitated for 30
 mins. to obtain the dispersion. (27ppW156NMSDwgNo0/0).

J61026608-A

(19) Japanese Patent Office (JP)

(12) Laid Open Patent Application Gazette (A)

(11) Laid Open Patent Application Number 61-26608

(43) Publication Date: 5th February 1986

(51) Int. Cl ⁴	Recogn. Code	Office Handling Number
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C 08 F 220/28 8319-4J

220/34 8319-4J

226/06 8319-4J

Request for Examination: Not yet requested

Number of Inventions: One

Number of Pages in the Japanese Text: Twenty seven

(54) Title of the Invention: Aqueous pigment
dispersions

(21) Application Number: 59-146994

(22) Date of Application: 17th July 1984

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SPECIFICATION

1. Title of the Invention

Aqueous pigment dispersions

2. Scope of the Patent Claims

An aqueous pigment dispersion comprising pigment, dispersant and aqueous medium, characterised in that the said dispersant comprises a polymeric water-soluble material which has been obtained by the copolymerisation of (A) from 3 to 98 parts by weight of (meth)acrylic monomer which has been modified with a substance selected from among (a) fatty acids, (b) lactones or oxy-acid condensates and (c) mono- or poly-alkylene glycols or mono-ether derivatives thereof, (B) from 2 to 97 parts by weight of α,β -ethylenic unsaturated nitrogen-containing monomer, (C) from 0.5 to 30 parts by weight of quaternary ammonium salt-containing (meth)acrylic monomer and (D) from 0 to 91 parts by weight of α,β -ethylenic unsaturated monomer other than those indicated in (A), (B) and (C) above.

3. Detailed Description of the Invention

The invention concerns aqueous pigment dispersions which are easily dispersed and have excellent dispersion stability in which a novel dispersant is used.

It was well known that in the past undesirable phenomena such as a reduction of the colouring effect of the paint surface, flooding, floating and a reduction in gloss, for example, due to difficulty with the dispersion of the pigment during production and aggregation and settling out of the pigment during storage arose with aqueous paints such as emulsion paints and water-soluble resin paints which contained pigments. Consequently, an aqueous pigment dispersion in which the pigment is pre-dispersed using a

dispersant has generally been prepared and this has been mixed with and dispersed in the coloured aqueous paint for colouring an aqueous paint.

Low molecular weight compounds such as surfactants have been used as the dispersants in these aqueous pigment dispersions in the past, but the adverse effects due to the dispersant, which is to say the secondary adverse effects such as a lowering of the paint film performance and the effect on the state of the paint film, cannot be avoided and, more recently, the lowering of paint film performance has been prevented by using oligomers or polymers of intermediate molecular weight as dispersants.

However, when oligomers and polymers are used as dispersants, the amount used is greater than the amount of low molecular weight surfactant which has been used in the past and there is a problem in that limitations are imposed on the use of the aqueous pigment dispersions which are obtained, depending on the type of binder which is being used in the aqueous paint. This is a retrograde step in terms of any rationalisation of the production of paints, and so the development of aqueous pigment dispersions which can be used commonly in all types of water-based paint is very desirable.

Thus, the inventors have realised the present invention as a result of thorough research carried out with a view to developing an ideal dispersant with which a pigment can be dispersed with the use of just a small amount, which is compatible with all types of aqueous resin, and which itself does not result in a lowering of the paint film performance of an aqueous paint, for use in an aqueous system where this has been especially difficult.

Thus, according to the present invention there is provided an aqueous pigment dispersion comprising pigment, dispersant and aqueous medium, characterised in that the said dispersant comprises a polymeric water-soluble material which has been obtained by the copolymerisation of (A) from 3 to 98 parts by weight of (meth)acrylic monomer (referred to hereinafter as a modified (meth)acrylic monomer) which has been modified with a substance selected from among (a) fatty acids, (b) lactones or oxy-acid condensates and (c) mono- or poly-alkylene glycols or mono-ether derivatives thereof, (B) from 2 to 97 parts by weight of α,β -ethylenic unsaturated nitrogen-containing monomer, (C) from 0.5 to 30 parts by weight of quaternary ammonium salt-containing (meth)acrylic monomer and (D) from 0 to 91 parts by weight of α,β -ethylenic unsaturated monomer other than those indicated in (A), (B) and (C) above.

The polymer which is used as a dispersant in an aqueous pigment dispersion of this invention has a structure which is non-crystalline with long side chains which include the hydrophilic quaternary ammonium salt groups and the comparatively hydrophilic nitrogen-containing compounds bonded in a state isolated from the main chain and so it is characterised in that it has a very high pigment dispersing capacity.

The dispersants which can be used in an aqueous pigment dispersion of this invention are described in detail below.

The Modified (Meth)acrylic Monomer A

The modified (meth)acrylic monomer (A) used in this invention is a modified (meth)acrylic acid monomer, which has a radically polymerisable group, selected from among (a) the fatty acid modified (meth)acrylic monomers, (b) the lactone or oxy-acid

condensate modified (meth)acrylic monomers and (c) the mono- or poly-alkylene glycol, or mono-ether derivative thereof, modified (meth)acrylic monomers.

The fatty acid modified (meth)acrylic monomers (a) which are used in the production of the above mentioned modified (meth)acrylic monomer (A) are monomers which have been produced by introducing a fatty acid, such as a drying oil fatty acid, semi-drying oil fatty acid, non-drying oil fatty acid or synthetic saturated fatty acid for example, into a (meth)acrylic monomer as described hereinafter using a method as described hereinafter. Here, the synthetic saturated fatty acids include the linear chain or branched chain saturated aliphatic carboxylic acids which have from 4 to 24, and preferably from 5 to 18, carbon atoms which have been derived artificially using the ozone oxidation method, the paraffin liquid-phase air-oxidation method, the oxo method, the Koch method or such like method from natural oils or fats, or from a fatty acid or petroleum raw material.

Typical examples of the fatty acids used to produce the above mentioned fatty acid modified (meth)acrylic monomers include drying oil or semi-drying oil fatty acids such as safflower oil fatty acid, linseed oil fatty acid, soy-bean oil fatty acid, sesame oil fatty acid, poppy oil fatty acid, perilla oil fatty acid, hemp-seed oil fatty acid, tall oil fatty acid, sunflower oil fatty acid, cotton seed oil fatty acid, walnut oil fatty acid, rubber seed oil fatty acid, tung oil fatty acid, oiticica oil, dehydrated castor oil fatty acid, high diene fatty acids and the like; non-drying oil fatty acids such as coconut oil fatty acid, olive oil fatty acid, castor oil fatty acid, hydrogenated castor oil fatty acid,

palm oil fatty acid and the like; and synthetic saturated fatty acids such as neopentanoic acid, 2-ethylbutyric acid, heptanoic acid, 2-ethylhexanoic acid, iso-octanoic acid, nonanoic acid, iso-nonanoic acid, decanoic acid, iso-decanoic acid, neo-decanoic acid, iso-tridecanoic acid, iso-palmitic acid, iso-stearic acid and the like, and these can be used individually, or a mixture of two or more types can be used.

The amount of the above mentioned fatty acid used can be varied over a wide range according to the drying properties and paint film performance required of the aqueous pigment dispersion which is provided by the invention, but in general the use of an amount within the range from 5 to 65 wt%, and preferably within the range from 10 to 60 wt%, with respect to the weight of the polymer (sic) obtained, is advantageous.

Furthermore, in this invention the drying oil fatty acids and semi-drying oil fatty acids which have an iodine value of at least about 100 from among the above mentioned fatty acids are ideal since it is then possible to impart crosslinking and drying properties at normal temperature to the dispersant obtained.

Esters of (meth)acrylic acid which contain functional groups, such as epoxy groups and hydroxyl groups, for example, which can react with the carboxyl groups of the said fatty acids, in the ester residual part can be cited as examples of the (meth)acrylic monomers into which these fatty acids can be introduced.

The (meth)acrylic acid esters which have an epoxy group (referred to hereinafter as epoxy-containing (meth)acrylic esters) are one type of (meth)acrylic monomer into which the aforementioned fatty acids can

be introduced to obtain a fatty acid modified (meth)acrylic monomer (a), and esters of this type include those which have a glycidyl group in the ester residual group of the (meth)acrylic acid, and glycidyl (meth)acrylate in particular is ideal. The preparation of a fatty acid modified (meth)acrylic monomer using such an epoxy-containing (meth)acrylic ester can be carried out by reacting a fatty acid as described above with the epoxy-containing (meth)acrylic ester in the presence or absence of the usual suitable inert solvents, and generally in the absence of a solvent. The said reaction can generally be carried out at a temperature of from about 60 to about 220°C, and preferably at a temperature of from about 120 to about 170°C, and the reaction time is generally from about 0.5 to about 40 hours, and preferably from about 3 to about 10 hours.

The said epoxy-containing (meth)acrylic ester is used advantageously in an amount generally of from 0.7 to 1.5 mol, and preferably in an amount of from 0.8 to 1.2 mol, per mol of the said fatty acid.

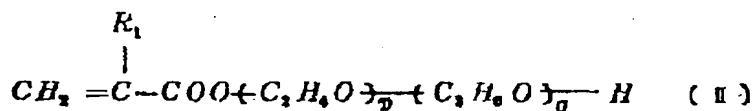
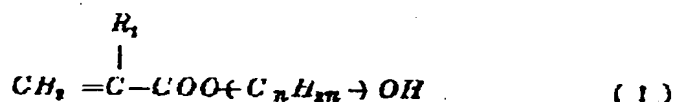
Furthermore, water-immiscible organic solvents which can reflux at a temperature below 220°C are preferred for the inert solvent which can be used, as required, and examples of such solvents include aromatic hydrocarbons such as benzene, toluene and xylene, and aliphatic hydrocarbons such as pentane, hexane and octane.

Moreover, polymerisation inhibitors, such as hydroquinone, methoxyphenol, tert-butylcatechol and benzoquinone for example, can be added to the reaction system, as required, in the above mentioned reaction, and this is advantageous for suppressing the polymerisation of the hydroxyl group (sic) containing

acrylic ester and/or the fatty acid modified (meth)acrylic ester which is being produced.

In the above mentioned reaction, esterification accompanied by ring opening of the oxylane group (epoxy group) occurs between the oxylane group of the epoxy-containing (meth)acrylic ester and the carboxyl group of the fatty acid and a (meth)acrylic ester which has been modified with fatty acid is obtained.

Furthermore, other different (meth)acrylic monomers which can be reacted with the above mentioned fatty acids to produce fatty acid modified (meth)acrylic monomers include (meth)acrylic acid esters which contain a hydroxyl group (referred to hereinafter as hydroxyl group-containing (meth)acrylic esters), and this type of ester includes those which have one hydroxyl group in the ester residual group of the (meth)acrylic acid ester and in which the said ester residual group has from 2 to 24, and preferably from 2 to 8, carbon atoms, and from among these the hydroxyl group-containing (meth)acrylic acid esters of the type represented by formula (1) or formula (2) below are ideal.



(In these formulae, R_1 represents a hydrogen atom or a methyl group, n is an integer of value from 2 to 8, p and q are each independent integers of value from 0 to 8, and the sum of p and q is from 1 to 8.)

The hydroxyalkyl acrylates and hydroxyalkyl methacrylates which can be represented by general formula (1) above, and from among these 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, 2-hydroxypropyl acrylate and 2-hydroxypropyl methacrylate, are especially desirable hydroxyl group-containing (meth)acrylic esters in this invention.

The preparation of fatty acid modified (meth)acrylic monomers of this latter type can be carried out by reacting the aforementioned fatty acids with the above mentioned hydroxyl group-containing (meth)acrylate esters in a suitable inert solvent in the presence of an esterification catalyst. The said reaction is carried out with heating generally at a temperature of from about 100 to about 180°C, and preferably of from about 120°C to about 160°C, and the reaction time is generally from about 0.5 to about 9 hours, and normally from about 1 to about 6 hours.

The said hydroxyl group-containing (meth)acrylic esters are used advantageously in an amount generally of from 0.5 to 1.9 mol per mol of the said fatty acid, and preferably in an amount of from 1.0 to 1.5 mol per mol of the said fatty acid.

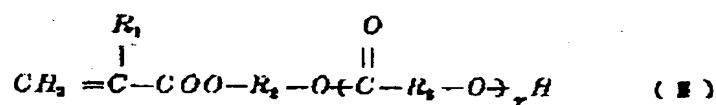
Examples of esterification catalysts which can be used in the above mentioned reaction include sulphuric acid, aluminium sulphate, potassium hydrogen sulphate, p-toluenesulphonic acid, methyl sulphate and phosphoric acid, and these catalysts are generally used in amounts of from about 0.001 to about 20 wt%, and preferably in amounts of from about 0.05 to about 10 wt%, with respect to the total amount of the above mentioned fatty acid and hydroxyl group-containing (meth)acrylic ester which are being reacted.

Furthermore, a water immiscible organic solvent which refluxes at a temperature below 180°C is preferred for the inert solvent which can be used, as required, and examples include aromatic hydrocarbons such as benzene, toluene and xylene, and aliphatic hydrocarbons such as heptane, hexane and octane.

Moreover, polymerisation inhibitors, such as hydroquinone, methoxyphenol, tert-butylcatechol and benzoquinone for example, can be added to the reaction system, as required, in the above mentioned reaction, and this is advantageous for suppressing the polymerisation of the hydroxyl group-containing acrylic ester and/or the fatty acid modified (meth)acrylic ester which is being produced.

Another different method for the preparation of the fatty acid modified (meth)acrylic monomer involves subjecting an unsaturated fatty acid glycidyl ester (for example "Purenma DFA" produced by the Nippon Yushi Co.) and acrylic acid or methacrylic acid to an esterification reaction in the same way as before.

The lactone or oxy-acid condensate modified (meth)acrylic monomers (b) (referred to hereinafter as lactone modified (meth)acrylic monomers or oxy-acid condensate modified (meth)acrylic monomers) which can be used in the production of a modified (meth)acrylic monomer (A) are monomers obtained by reacting lactone or oxy-acid condensate with a (meth)acrylic monomer, and typical examples include those which can be represented by the formula (III) below.



(In this formula R_1 has the same significance as before, R_2 represents a $-C_aH_{2a}-$ group (where a is an integer of value from 2 to 8) or a $-CH_2-CH(R_1)(OH)-CH_2-$ group (where R_1 has the same significance as before), R_2 represents a $-C_bH_{2b}-$ group (where b is an integer of value from 2 to 18), and r is from 1 to 7.)

The lactone used as the modifying agent for a modified (meth)acrylic monomer which can be represented by formula (III) above is a cyclic ester compound which has an ester functional group, $-CO-O-$, within the ring, and typical examples include γ -lactone, δ -lactone, ϵ -lactone, γ -caprolactone, δ -caprolactone and methyl- ϵ -caprolactone (isomers also included).

Furthermore, the oxy-acid condensates are condensates of aliphatic mono-carboxylic acids which have one hydroxyl group within the molecule (hydroxy-fatty acids), and examples of the said hydroxy-fatty acids include the ring-opened forms of the aforementioned lactones, recinoleic acid, oxy-stearic acid and lanopalmic acid. The production of these oxy-acid condensates can be carried out in the usual way by heating and condensing a mixture comprising the aforementioned hydroxy-fatty acids, a refluxing solvent (xylene, toluene, heptane or the like) and an esterification catalyst (methyl sulphate, dodecylbenzene sulphonic acid and the like) at a temperature of from about 140°C to about 250°C .

The aforementioned lactone compound or oxy-acid condensate can be introduced into a (meth)acrylic monomer in the ways indicated below. When they are being introduced, the above mentioned lactone compounds or oxy-acid condensates may be used individually, or a combination of two or more types can be used.

The hydroxyl group-containing (meth)acrylic esters represented by the aforementioned formula (I) can be used ideally as (meth)acrylic monomers into which the aforementioned lactone compounds are introduced to obtain a lactone modified (meth)acrylic monomer. The preparation of a lactone modified (meth)acrylic monomer using a hydroxyl group-containing (meth)acrylic ester of this type can be carried out using a known method, such as the method disclosed in Japanese Unexamined Patent Application Laid Open 57-195714 for example, and it is generally carried out by reacting the aforementioned lactone and hydroxyl group-containing (meth)acrylic ester at a temperature of from about 20 to 220°C, and preferably of from about 50 to 180°C, in the presence of a catalyst. The reaction time is generally from about 0.5 to 40 hours, and preferably from about 5 to 20 hours. Organo-tin compounds, alkyl titanates, lead compounds and acid catalysts, for example, can be used for the catalyst.

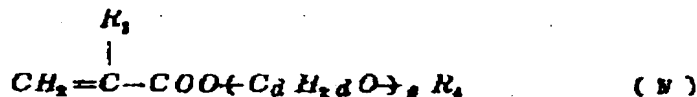
A molecular weight of from 200 to 1500, and preferably of from 400 to 1000, is desirable for the lactone modified (meth)acrylic monomers obtained in this way, and adjustment of the molecular weight can be carried out easily by changing appropriately the compounding ratio of the lactone and the hydroxyl group-containing (meth)acrylic ester.

Furthermore, the aforementioned containing (sic) methacrylic esters are used ideally in the production of the epoxy (sic) fatty acid modified (meth)acrylic monomers as the (meth)acrylic monomers into which the aforementioned oxy-acid condensates are introduced for obtaining an oxy-acid condensate modified (meth)acrylic monomer.

The preparation of such oxy-acid condensate modified (meth)acrylic monomers can be carried out by reacting the aforementioned oxy-acid condensates with the aforementioned epoxy-containing (meth)acrylic esters. The said reaction can be carried out in the same way as the reaction of the fatty acids and epoxy-containing (meth)acrylic esters in the preparation of the aforementioned fatty acid modified (meth)acrylic monomers.

The said epoxy-containing (meth)acrylic esters are generally used advantageously in an amount of from 0.7 to 1.5 mol, and preferably in an amount of from 0.8 to 1.2 mol, per mol of the said oxy-acid condensate. Moreover, the said oxy-acid condensate advantageously has a molecular weight generally of from about 100 to 2500, and preferably of from about 200 to 2000.

Moreover, the (meth)acrylic monomer which has been modified with mono- or poly-alkylene glycol, or a mono-ether derivative thereof, (referred to hereinafter as an alkylene glycol modified (meth)acrylic monomer) which is used in the production of a modified (meth)acrylic monomer (A) is, for example, (meth)acrylic acid which has been esterified with mono- or poly-alkylene glycol, or a mono-ether derivative thereof, and typically those which can be represented by the general formula (IV) indicated below are included.



(In this formula R_1 has the same significance as before, R_4 represents a hydrogen atom, a C_1 to C_{20} alkyl group, an aryl group (for example a phenyl group) or an

aralkyl group (and preferably a benzyl group), d is an integer of value from 2 to 12 and e is an integer of value from 1 to 20.)

Actual examples of such alkylene modified (meth)acrylic monomers include diethylene glycol (meth)acrylate, triethylene glycol (meth)acrylate, polyethylene glycol (meth)acrylate, dipropylene glycol (meth)acrylate, tripropylene glycol (meth)acrylate, polypropylene glycol (meth)acrylate, methoxyethylene (meth)acrylate, ethoxyethylene (meth)acrylate, butoxyethylene (meth)acrylate, hexyloxyethylene (meth)acrylate, ethoxypropylene (meth)acrylate, ethoxydiethylene (meth)acrylate, propoxydiethylene (meth)acrylate, butoxydiethylene (meth)acrylate, dodecyloxydiethylene (meth)acrylate, phenoxydipropylene (meth)acrylate and benzyloxydiethylene (meth)acrylate, and these may be used individually, or a combination of two or more types may be used. Furthermore, advantageously the molecular weight of these alkylene modified (meth)acrylates is generally within the range from 100 to 5000, and preferably within the range from 150 to 1500.

The α,β -Ethylenic Unsaturated Nitrogen-containing Monomer (B):

The α,β -ethylenic unsaturated nitrogen-containing monomers (B) used in the invention include monomers which contain one basic nitrogen atom, or a plurality (generally up to four) of basic nitrogen atoms, and one ethylenic unsaturated bond in a single molecule, and typical examples include unsaturated monomers which have a nitrogen-containing heterocyclic ring and nitrogen-containing derivatives of (meth)acrylic acid. These monomers are described in more practical terms below.

[1] Monomers in which a monocyclic or polycyclic heterocyclic ring which contains from 1 to 3, and preferably 1 or 2, ring nitrogen atoms, is bonded to a vinyl group are included among the unsaturated monomers which have a nitrogen-containing ring, and the monomers indicated below can be cited as actual examples.

(i) Vinylpyrrolidones

For example, 1-vinyl-2-pyrrolidone, 1-vinyl-3-pyrrolidone and the like.

(ii) Vinylpyridines

For example, 2-vinylpyridine, 4-vinylpyridine, 5-methyl-2-vinylpyridine, 5-ethyl-2-vinylpyridine and the like.

(iii) Vinylimidazoles

For example, 1-vinylimidazole, 1-vinyl-2-methylimidazole and the like.

(iv) Vinylcarbazoles

For example, N-vinylcarbazole and the like.

(v) Vinylquinolines

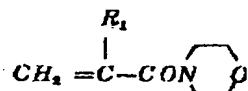
For example, 2-vinylquinoline and the like.

(vi) Vinylpiperidines

For example, 3-vinylpiperidine, N-methyl-3-vinylpiperidine and the like.

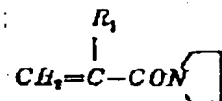
(vii) Others

For example, the N-(meth)acryloylmorpholines which can be represented by the formula:



(where R₁ has the same significance as before)

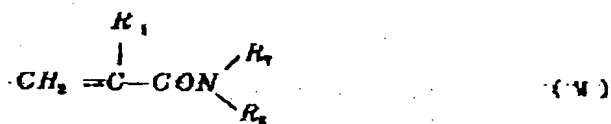
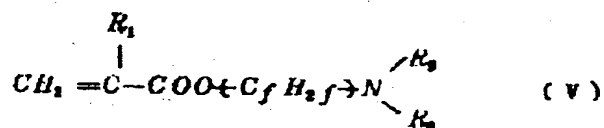
and the N-(meth)acryloylpyrrolidines which can be represented by the formula:



(where R_1 has the same significance as before.)

From among the above mentioned vinyl monomers which have nitrogen-containing rings the vinylpyrrolidones, vinylimidazoles and vinylcarbazoles are preferred, and those among these compounds where the ring nitrogen atom is a tertiary nitrogen atom are ideal.

[2] The monomers where a substituted or unsubstituted amino group is included in the ester part of a (meth)acrylic acid ester and the amides of (meth)acrylic acid are included among the nitrogen-containing derivatives of (meth)acrylic acid, and the aminoalkyl (meth)acrylates and the (meth)acrylamides which can be represented by formulae (V) and (VI) below are especially desirable.



(In these formulae R_5 and R_6 each independently represent a hydrogen atom or a lower alkyl group, R_7 represents a hydrogen atom or a lower alkyl group, R_8 represents a hydrogen atom, a lower alkyl group, a di-(lower alkyl)amino lower alkyl group, a hydroxy-lower alkyl group or a lower alkoxy-lower alkyl group, R_1 has the same significance as before and f is an integer of value from 2 to 8.)

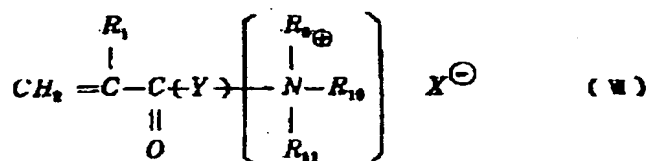
Moreover, the term "lower" as used in this specification signifies that the group which is so designated has not more than six, and preferably not more than four, carbon atoms.

Actual examples of such nitrogen-containing (meth)acrylic monomers include N,N-dimethylaminoethyl (meth)acrylate, N,N-diethylaminoethyl (meth)acrylate, N-t-butylaminoethyl (meth)acrylate, N,N-dimethylamino-propyl (meth)acrylate, N,N-dimethylaminobutyl (meth)-acrylate, N-propylaminoethyl (meth)acrylate and N-butylaminoethyl (meth)acrylate as examples of the aminoalkyl (meth)acrylates represented by the above mentioned formula (V), and (meth)acrylamide, N-methyl(meth)acrylamide, N-ethyl(meth)acrylamide, N-butyl(meth)acrylamide, N,N-dimethyl(meth)acrylamide, N,N-diethyl(meth)acrylamide, N,N-dipropyl(meth)-acrylamide, N-methylol(meth)acrylamide, N-ethoxymethyl-(meth)acrylamide, N-butoxymethyl(meth)acrylamide and N,N-dimethylaminopropylacrylamide are included as examples of the (meth)acrylamides of the above mentioned formula (VI). These nitrogen-containing (meth)acrylic monomers ideally have the nitrogen atoms which are present in the tertiary form, and the compounds where the nitrogen atoms which are present are in the secondary form can also be used ideally.

The α,β -ethylenic unsaturated nitrogen-containing monomers described above can be used individually, or a combination of two or more types can be used.

The Quaternary Salt-containing (Meth)acrylic Monomer (d) (sic):

Monomers which have one quaternary ammonium salt group and one (meth)acryloyl group in a single molecule are included among the quaternary ammonium salt-containing (meth)acrylic monomers used in this invention, and those which can be represented by the general formula (VII) indicated below are ideal.



(In this formula R_1 has the same significance as before, Y represents $-\text{O}-$, a C_gH_{2g} group (where g is an integer of value from 2 to 8), an $-\text{O}-\text{CH}_2-\text{CH}(\text{OH})-\text{CH}_2-$ group or an $-\text{N}(\text{R}_{12})-\text{C}_g\text{H}_{2g}-$ group (where R_{12} represents a hydrogen atom or a lower alkyl group and g has the same significance as before), R_9 , R_{10} and R_{11} each independently represent a lower alkyl group, a hydroxy-lower alkyl group, a lower alkoxy-lower alkyl group, a cycloalkyl group, a substituted or unsubstituted phenyl group or an alkyl group (sic), and X represents an anion.)

Halogen ions and the residual anions of acids are included among the anions represented by X in this formula, and actual examples of the anion include Cl^- , Br^- , I^- , F^- , HSO_4^- , SO_4^{2-} , NO_3^- , PO_4^{3-} , HPO_4^{2-} , H_2PO_4^- , $\text{C}_6\text{H}_5\text{SO}_3^-$ and OH^- , and Cl^- , Br^- and SO_4^{2-} are preferred.

Typical examples of such quaternary ammonium salt-containing (meth)acrylic monomers include 2-hydroxy-3-(meth)acryloxypropyltrimethylammonium chloride, 2-hydroxy-3-(meth)acryloxypropyltributylammonium chloride, 2-hydroxy-3-(meth)acryloxypropyltriethanolammonium chloride, 2-hydroxy-3-(meth)acryloxypropyldimethylbutylammonium chloride, 2-hydroxy-3-(meth)acryloxypropyldimethylphenylammonium chloride, (meth)acryloxyethyltrimethylammonium chloride and (meth)acrylamidopropyltrimethylammonium chloride, and these may be used individually, or a combination of two or more types can be used.

The Other α, β -Ethylenic Unsaturated Monomer (D)

No particular limitation is imposed upon the α,β -ethylenic unsaturated monomer other than the above mentioned components (A) to (C), which is to say the monomer (D), and this component can be selected from among a wide range of monomers in accordance with the performance required of the dispersant of this invention. Some typical examples of such unsaturated monomers are indicated below.

(a) Acrylic Acid or Methacrylic Acid Esters:

For example, C_1 to C_{16} alkyl esters of acrylic acid or methacrylic acid such as methyl acrylate, ethyl acrylate, propyl acrylate, isopropyl acrylate, butyl acrylate, hexyl acrylate, octyl acrylate, lauryl acrylate, methyl methacrylate, ethyl methacrylate, propyl methacrylate, isopropyl methacrylate, butyl methacrylate, hexyl methacrylate, octyl methacrylate and lauryl methacrylate; glycidyl acrylate and glycidyl methacrylate; C_2 to C_6 alkenyl esters of acrylic acid or methacrylic acid such as allyl acrylate and allyl methacrylate; C_2 to C_6 hydroxyalkyl esters of acrylic acid or methacrylic acid such as hydroxyethyl acrylate, hydroxyethyl methacrylate, hydroxypropyl acrylate and hydroxypropyl methacrylate; and C_2 to C_{16} alkenyloxy-alkyl esters of acrylic acid or methacrylic acid such as allyloxyethyl acrylate and allyloxy methacrylate (sic).

(b) Vinyl Aromatic Compounds:

For example, styrene, α -methylstyrene, vinyl-toluene and p-chlorostyrene.

(c) Polyolefinic Compounds:

For example, butadiene, isoprene and chloroprene.

(d) Others:

Acrylonitrile, methacrylonitrile, methyl isopropenyl ketone, vinyl acetate, "Peoba" monomer

(product of the Shell Chemical Co.), vinyl propionate, vinyl pivalate and the like.

These unsaturated monomers can be selected appropriately in accordance with the properties required, and they can be used individually, or a combination of two or more types can be used.

According to the present invention, the above mentioned modified (meth)acrylic monomer (A), α,β -ethylenic unsaturated nitrogen-containing monomer (B), quaternary ammonium salt-containing (meth)acrylic monomer (C) and α,β -ethylenic unsaturated monomer (D) are copolymerised. The said copolymerisation can be carried out in accordance with the known methods for the production of acrylic copolymers using, for example, the solution polymerisation method, the emulsification polymerisation method or the suspension polymerisation method.

The compounding proportions of the four components indicated above when carrying out the copolymerisation can be varied according to the performance required as a dispersant, but compounding within the proportions indicated below is appropriate.

Modified (Meth)acrylic Monomer (A):

From 3 to 98 parts by weight, and preferably from 10 to 85 parts by weight from the viewpoint of the paint film performance.

α,β -Ethylenic Unsaturated Nitrogen-containing
Monomer (B):

From 2 to 97 parts by weight, and preferably from 3 to 90 parts by weight from the viewpoint of pigment dispersion.

Quaternary Ammonium Salt-Containing (Meth)acrylic
Monomer (C):

From 10.5 to 30 parts by weight, and preferably from 1 to 18 parts by weight from the viewpoints of water solubility and paint film performance.

Unsaturated Monomer (D) Other than (A) to (C) Above:

From 0 to 91 parts by weight, and preferably from 5 to 83 parts by weight from the viewpoint of the paint film performance.

Advantageously, the above mentioned polymerisation reaction is preferably carried out using the solution polymerisation method, and this can be carried out by reacting the four components mentioned above in a suitable inert solvent in the presence of a polymerisation catalyst at a reaction temperature generally of from about 0 to about 180°C, and preferably of from about 40 to about 170°C, for a period of from about 1 to about 20 hours, and preferably of from about 6 to about 10 hours.

The use of a solvent in which the copolymer which is produced dissolves and which is miscible with water is preferred for the solvent so that gelling does not occur during the said copolymerisation reaction. A solvent which need not be removed when obtaining the aqueous pigment dispersion is especially desirable. Examples of such solvents include cellosolve-based solvents of formula $\text{OH}-\text{CH}_2\text{CH}_2-\text{OR}_{13}$ (where R_{13} signifies a hydrogen atom or an alkyl group which has from 1 to 8 carbon atoms) such as ethylene glycol, butylcellosolve and ethylcellosolve for example; propylene glycol-based solvents of formula $\text{HOCH}_2-\text{CH}(\text{CH}_3)-\text{OR}_{13}$ (where R_{13} has the same significance as before) such as propylene glycol monomethyl ether for example; carbitol-based solvents of formula $\text{OH}-\text{CH}_2\text{CH}_2-\text{OCH}_2\text{CH}_2-\text{OR}_{13}$ (where R_{13} has the same significance as before) such as diethylene glycol, methylcarbitol and butylcarbitol for example; glyme-

based solvents of formula $R_{14}O-CH_2CH_2-OR_{15}$ (where R_{14} and R_{15} each independently represent an alkyl group which has from 1 to 3 carbon atoms) such as ethylene glycol dimethyl ether for example; diglyme-based solvents of formula $R_{14}O-CH_2CH_2OCH_2-CH_2R_{15}$ (where R_{14} and R_{15} have the same significance as before) such as diethylene glycol dimethyl ether for example; cellosolve acetate-based solvents of formula $R_{16}O-CH_2CH_2OCO-CH_3$ (where R_{16} represents a hydrogen atom, CH_3 or C_2H_5) such as ethylene glycol mono-acetate and methyl cellosolve acetate for example; alcohol-based solvents of formula $R_{17}OH$ (where R_{17} represents an alkyl group which has from 1 to 4 carbon atoms) such as ethanol and propanol for example; and diacetone alcohol, dioxane, tetrahydrofuran, acetone, dimethylformamide, 3-methoxy-3-methylbutanol and such like solvents can be used.

However, inert solvents which are immiscible with water can also be used, and those of boiling point below $250^{\circ}C$ so that they can be removed easily by distillation at normal pressure or under reduced pressure after the polymerization reaction has been completed are preferred as such water-immiscible solvents. Examples of such solvents include aromatic hydrocarbons which can be represented by the formula $\phi-R_{18}$ (where ϕ represents a benzene ring and R_{18} represents a hydrogen atom or an alkyl group which has from 1 to 4 carbon atoms) or the formula $R_{19}-\phi-R_{20}$ (where ϕ represents a benzene ring and R_{19} and R_{20} each represent an alkyl group which has from 1 to 4 carbon atoms which may be substituted at any position) such as toluene and the xylenes for example; acids or esters of formula $R_{21}-COO-R_{22}$ (where R_{21} represents an alkyl group which has from 1 to 6 carbon atoms and R_{22} represents a hydrogen atom or an alkyl group which has from 1 to 6

carbon atoms) such as acetic acid, ethyl formate, ethyl acetate and cyclohexyl acetate for example; ketones which can be represented by the formula $R_{23}R_{24}C=O$ (where R_{23} and R_{24} each independently represent an alkyl group which has from 1 to 8 carbon atoms or by the formula $C_6H_{10}=O$ (where C_6H_{10} is a cyclohexane residual group), such as methyl ethyl ketone and cyclohexanone for example; ethers which can be represented by the formula $R_{23}-O-R_{24}$ (where R_{23} and R_{24} have the same significance as before) such as ethyl ether and hexyl ether for example; and alcohols which can be represented by the formula $R_{25}OH$ (where R_{25} represents an alkyl group which has from 5 to 11 carbon atoms) such as hexanol for example.

These solvents can be used in amounts within the range from 15 to 90 wt% of the total amount of the four components of the aforementioned copolymer.

Furthermore, the radical polymerisation initiators used for radical polymerisation, such as azo compounds, peroxide compounds, sulphides, sulphines, sulphinic acids, diazo compounds, nitroso compounds, redox systems and ionising radiation, for example, can be used for the polymerisation initiator.

In this invention, an aqueous pigment dispersion which is satisfactory in practice can be obtained even if the molecular weight of the copolymer which is produced varies, but if the molecular weight is too low then it is possible that the properties of a painted film obtained with a coloured aqueous paint may be adversely affected. Furthermore, if the molecular weight is too high then the viscosity rises, and if the viscosity is reduced then the copolymer concentration is reduced and the dispersibility of the pigment is adversely affected, and so the aforementioned

copolymerisation reaction is advantageously carried out generally until the number average molecular weight of the copolymer which has been produced is within the range from about 500 to about 150000, and preferably within the range from about 1000 to about 100000.

Water is added to the copolymer resin which has been produced in this way, with or without removing the solvent, to form an aqueous solution.

The polymer aqueous solution obtained in this way can be used as a dispersant for an aqueous pigment dispersion comprising pigment, dispersant and aqueous medium.

The amount of dispersant comprising the above mentioned polymer aqueous solution used is generally from about 1 to 500 parts by weight, and preferably from about 1 to 300 parts by weight, per 100 parts by weight of pigment. If the upper limit of this range is exceeded then the balance of the viscosity and colouring capacity of the aqueous pigment dispersion tends to be lost, while if it falls below the lower limit then the dispersion stability of the pigment is liable to fall.

The aqueous medium which is used in the aqueous pigment dispersion is essentially water, but in those cases where the affinity for water of the dispersant is low, for example, and a satisfactory pigment dispersing capacity cannot be achieved, a hydrophilic organic solvent can be used conjointly, as required. The solvents used in the production of the aforementioned polymer can be used individually or in the form of mixtures for the said hydrophilic organic solvent.

Furthermore, the pigments which can be used in an aqueous pigment dispersion of this invention include the inorganic and organic pigments which are generally

used in pigment dispersions of this type, and actual examples of inorganic pigments include (1) oxide pigments (such as flowers of zinc, titanium dioxide, red iron oxide, chromium oxide, cobalt blue and iron black for example); (2) hydroxide pigments (such as alumina white and yellow iron oxide for example); (3) sulphides and selenides (such as zinc sulphide, cinnabar, cadmium yellow and cadmium red for example); (4) ferrocyanides (such as Prussian blue for example); (5) chromates (such as copper yellow, zinc chromate and molybdenum red for example); (6) sulphates (such as precipitated barium sulphate for example); (7) carbonates (such as precipitated calcium carbonate for example); (8) silicates (such as hydrated silicates, clay and ultramarine for example); (9) phosphates (such as manganese violet for example); (10) carbon (such as carbon black for example); and (11) metal powders (such as aluminium powder, bronze powder and zinc powder for example), and organic pigments such as (1) nitroso pigments (such as naphthol green B for example); (2) nitro pigments (such as naphthol yellow S for example); (3) azo pigments (such as lithol red, lake red C, fast yellow and naphthol red for example); (4) dye lake pigments (such as alkali blue lake and rhodamine lake for example); (5) phthalocyanine pigments (such as phthalocyanine blue and fast sky blue for example) and (6) condensed polycyclic pigments (such as perylene red, quinacridone red, dioxazine violet and isoindolinone yellow for example).

The amount of the aforementioned pigment included in an aqueous pigment dispersion of this invention is not subjected to any particular technical limitation, but it is generally from about 2 to 90 wt% based on the weight of the said dispersion.

The preparation of an aqueous pigment dispersion of this invention can be carried out by mixing together the various components indicated above in appropriate dispersing apparatus, and examples of dispersing apparatus which can be used include the ball mills, roll mills, homogenisers, sand grinders, shakers and attriters, for example, which are generally used in the paint industry.

Moreover, it is possible to improve the dispersion stability by adding the well-known surfactants and protective colloids to a cationic aqueous pigment dispersion of this invention as required.

A cationic aqueous pigment dispersion of this invention which has been obtained in this way has the pigment dispersed in a very uniform and finely divided state and even on long term storage there is virtually no aggregation or settling out of the pigment particles.

Thus, a cationic aqueous pigment dispersion of this invention has good miscibility with the water-soluble resins, water-dispersible resins and emulsions, for example, well known in the past, such as the alkyd resins, acrylic resins, epoxy resins, urethane resins, and maleinised polybutadiene resins which are used in aqueous paints and aqueous inks, and they can be used widely as colorants for aqueous paints comprising any resin, no limitation at all being imposed by the resin.

The proportion with respect to the aqueous paint of the cationic aqueous resin dispersion of the invention which is compounded therein can be varied widely in accordance with the type of pigment in the said dispersion and the degree of coloration ultimately required in the paint, but generally it can be

compounded in an amount within the range from about 2 to about 1000 parts by weight per 100 parts by weight of resin fraction in the aforementioned aqueous paint.

The invention is described in more detail below by means of illustrative examples. In these illustrative examples the terms "parts" and "%" signify "parts by weight" and "wt%".

Example of the Production of Fatty Acid Modified Acrylic Monomer (a)

Safflower oil fatty acid	236 parts
Glycidyl methacrylate	119 parts
Hydroquinone	0.4 part
Tetraethylammonium bromide	0.2 part

The components indicated above were introduced into a reactor and an addition reaction was carried out while stirring the reaction mixture and maintaining a reaction temperature of from 140 to 150°C. The addition reaction between the epoxy groups and the carboxyl groups was monitored by measuring the amount of residual carboxyl group. The fatty acid modified acrylic monomer (a) was obtained with a reaction time of about 4 hours.

Example of the Production of Fatty Acid Modified Acrylic Monomer (b)

Safflower oil fatty acid	70.9 parts
Hydroquinone	0.03 part
n-Heptane	4.56 parts

The components indicated above were introduced into a reactor and the temperature was raised to 160°C while stirring the mixture.

Hydroxyethyl methacrylate	41.2 parts
Hydroquinone	0.03 part
Dodecylbenzenesulphonic acid	0.95 part
Toluene	3.7 parts

A mixture comprising the components indicated above was then added dropwise over a period of 2 hours while maintaining the reactor at 160°C. The water produced by the condensation was removed from the reaction system and when the acid value of the reaction product had reached 5.5 and the Gardner viscosity had become A₂, the pressure within the reactor was reduced and the toluene and n-heptane were removed under reduced pressure and the fatty acid modified acrylic monomer (b) of acid value 5.0 and Gardner viscosity A₁ was obtained.

Example of the Production of Fatty Acid Modified Acrylic Monomer (c)

Iso-nonanoic acid	133 parts
Glycidyl methacrylate	119 parts
Hydroquinone	0.3 part
Tetraethylammonium bromide	0.2 part

An addition reaction of the above mentioned components was carried out under the same conditions as in the aforementioned example of the production of fatty acid modified acrylic monomer (a) and fatty acid modified acrylic monomer (c) was obtained.

Example of the Production of Fatty Acid Modified Acrylic Monomer (d)

Iso-palmitic acid	61.8 parts
Hydroquinone	0.03 part
n-Heptane	4.56 parts

The components indicated above were introduced into a reactor and the temperature was raised to 160°C while stirring the mixture.

Hydroxyethyl methacrylate	41.2 parts
Hydroquinone	0.03 part
Dodecylbenzenesulphonic acid	0.95 part
Toluene	3.7 parts

A mixture comprising the components indicated above was then added and reaction and removal under reduced pressure were carried out under the same conditions as in the aforementioned example of the production of fatty acid modified acrylic monomer (b) and the fatty acid modified acrylic monomer (d) of acid value 5.0 and Gardner viscosity A₁ was obtained.

Example of the Production of Oxy-acid Condensate Modified Acrylic Monomer (e)

12-Hydroxystearic acid	2155 parts
Toluene	383 parts
Monomethylsulphonic acid	4.3 part

These components were introduced into a reactor and reaction was carried out for 4 hours at 145°C while removing the water which was being produced by the condensation from the reaction system. When the resin acid value reached 34.0, 221 parts of glycidyl methacrylate, 2 parts of hydroquinone and 10 parts of tetraethylammonium bromide were added and reacted for 6 hours at a reaction temperature of 145°C, and oxy-acid condensate modified acrylic monomer (e) of resin acid value 5.8 was obtained.

Examples of the Preparation of Copolymer Solutions (a) to (u) for Dispersant Purposes

n-Butylcellosolve (350 parts) was introduced into a reactor and heated to 120°C. Next, a mixture of which the composition is indicated below was added dropwise into this liquid over a period of about 2 hours. This reaction was carried out under a blanket of nitrogen.

Fatty acid modified acrylic monomer (a)	118 parts
N-Vinylpyrrolidone	126 parts
50% Methacryloxyethyltrimethylammonium chloride aqueous solution	6 parts
Azobisdimethylvaleronitrile	17.5 parts

The above mentioned mixture was added dropwise while maintaining a reaction temperature of 80°C and stirring the reaction mixture. Azobisisobutyronitrile (2.5 parts) was added to the reaction mixture 1 hour after the drip feed had been completed and then 2.5 g of azobisisobutyronitrile were added to the reaction mixture after a further 2 hours and the reaction was continued while maintaining the temperature at 80°C for a further period of 2 hours. After the reaction had been completed the unreacted monomer and n-butylcellosolve were distilled off under reduced pressure and a copolymer solution (a) for dispersant purposes of residue on heating 70.1% and Gardener viscosity (40% n-butylcellosolve solution) I was obtained.

Polymerisation reactions and reduced pressure distillation were carried out in the same way under the same conditions as in the example of the production of copolymer solution (a) for dispersant purposes using the formulations shown hereinafter in Table 1 and the copolymer solutions (b) to (u) for dispersant purposes were obtained. A summary of the properties of the copolymer solutions (a) to (u) for dispersant purposes is shown hereinafter in Table 1.

Examples of the Production of an Aqueous Pigment Dispersion (1) to (33)

Water was added to the aforementioned copolymer solution (a) for dispersant purposes and the aqueous dispersant (A) comprising an aqueous solution of residue on heating 40% was obtained. The aqueous dispersants (B) to (U) were obtained in the same way by forming aqueous solutions of each of the aforementioned copolymer solutions (b) to (u) for dispersant purposes respectively.

Next water was added to a mixture of 8.3 parts of the aqueous dispersant (A) and 200 parts of titanium white pigment (Titanium White R-5N, produced by the Sakai Chemical Co.) and dispersed for 0.5 hours using a Red Devil dispersing machine and aqueous pigment dispersion (1) of this invention was obtained.

Aqueous pigment dispersions (2) to (33) of this invention were obtained by carrying out the dispersion of pigment in the same way using the formulations shown hereinafter in Tables 2 to 5. Moreover, the pigments other than titanium white were dispersed with a dispersion time of 1 hour.

A summary of the properties of the aqueous pigment dispersions obtained is shown hereinafter in Tables 2 to 5.

Examples 1 to 41

The combinations of the aqueous pigment dispersions (1) to (33) obtained in the aforementioned examples of production with the aqueous dispersion type cationic resins or cationic emulsions shown in Tables 6 to 9 were mixed thoroughly to prepare aqueous paints and the aqueous paints of Examples 1 to 41 were obtained. A summary of the performance of the paint films obtained using the aqueous paints so obtained is shown hereinafter in Tables 6 to 9.

Table 1

Copolymer Solution for Dispersant Purposes												
Modified Acrylic Monomer (A)	Fatty acid modified acrylic monomer				Oxy-acid condensate modified monomer				Other Monomer (D)			
	(a)	(b)	(c)	(d)	(e)	(f)	(g)	(h)	(i)	(j)	(k)	(l)
α , β -Ethylene Unsaturated Nitrogen-containing Monomer (B)	Fatty acid modified acrylic monomer (a)	118		90	90	96	99	102				
	" (b)		81									
	" (c)							119		96		
	" (d)								80			117
	Praxel FM-3 ¹											
	" FM-5 ²											
	Oxy-acid condensate modified monomer (e)											
	Purenu PE-350 ³											
	Purenu PP-1000 ⁴											
	NK Ester A-2PG ⁵											
Quaternary Ammonium Salt-containing Acrylic Monomer	N-vinylpyrrolidone	126	125	150				126	125			
	2-Vinylpyridine			150						150		
	N-Vinylcarbazole				150							126
	1-Vinylimidazole					143						
	N-Methacryloylmorpholine											
	N-Methacryloylpyrrolidine						143					
	N,N-Dimethylacrylamide											
	N,N-Dimethylaminoethyl methacrylate											
	Monomer ⁶	6	5	10	10	4	8	5	6	4	7	
	(I) (II) (III)											
Polymerisation Catalyst	n-Butyl methacrylate		39									
	Azobisdimethylvaleronitrile	17.5	18	17.7	"	"	"	"	18	17.5	"	
	"	2.5/2.5	"	"	"	"	"	"	"	"	"	
Properties	Heating Component (sic) (%)	70.1	70.8	70.4	71.0	70.8	70.5	71.0	70.4	71.5	71.0	
	Gardner Viscosity ⁷	I	K	L	M	H	N	O	D	E	G	

Table 1 (Continued)

Table 2

Item	Aqueous Pigment Dispersion									
Aqueous Dispersant	(A)	8.3	16.2	7.5	8.0					
	(B)				8.3					
	(C)					8.3				
	(D)						8.3			
	(E)							8.3		
	(F)								8.3	
	(G)									8.3
Pigment ⁸	Titanium White R-5N	200				200	200	200	200	200
	Carbon MA		60	90						
	Copper phthalocyanine green 6YK									
Properties	Yellow GKZR-8				85					
	Pigment/Dispersant (solid fraction ratio by weight)	60/1	9/1	30/1	27/1	60/1	60/1	60/1	60/1	60/1
	Pigment content (%)	74.8	27.5	52.2	54.8	75.0	74.9	74.8	74.7	74.8
	Particle size ⁹ (μ)	5	5	5	5	5	5	5	5	5
	Viscosity (60 rpm) Poise	38.2	6.2	8.0	24.0	36.0	30	32.5	15.3	33.0

Table 3

Item	Aqueous Pigment Dispersion															
Aqueous Dispersant	(H)	8.3		16.2		7.5		8.0								
	(I)															
	(J)													8.3		
	(K)														8.3	
Pigment ⁸	Titanium White R-5N	200											200	200	200	
	Carbon MA			60								90				
	Copper phthalocyanine green 6YK															
	Yellow GKZR-8												85			
Properties	Pigment/Dispersant (solid fraction ratio by weight)	60/1	9/1	9/1		30/1		27/1		60/1		60/1	60/1	60/1	60/1	
	Pigment content (%)	74.8		34.4		60.3		64.5		74.7		74.6	74.8	74.8	74.8	
	Particle size ⁹ (μ)	5	5	5		5		5		5		5	5	5	5	
	Viscosity (60 rpm) Poise	30.0		15.0		17.3		11.3		19.3		12.3	12.3	15.3	15.3	

Table 4

Item	Aqueous Pigment Dispersion															(25)
Aqueous Dispersant	(L)	8.3	16.2	7.5	8.0											
	(M)				8.3											
	(N)					8.3										
	(O)															
	(P)															8.3
Pigment ¹⁸	Titanium White R-5N	200														200
	Carbon MA		60													
	Copper phthalocyanine green 6YK			90												
	Yellow GK2R-8				85											
	Pigment/Dispersant (solid fraction ratio by weight)	60/1	9/1	30/1	27/1	60/1										60/1
Properties	Pigment content (%)	74.8	34.0	60.0	64.6	74.5										74.0
	Particle size ¹⁹ (μ)	5	5	5	5	5										5
	Viscosity (60 rpm) Poise	13.3	17.3	4.2	8.5	16.7										6.0

Table 5

Item	Aqueous Pigment Dispersion															(33)
Aqueous Dispersant	(Q)	8.3	16.2	7.5	8.0											
	(R)				8.3											
	(S)					8.3										
	(T)															
	(U)															8.3
Pigment ¹⁸	Titanium White R-5N	200														200
	Carbon MA		60													
	Copper phthalocyanine green 6YK			90												
	Yellow GK2R-8				85											
	Pigment/Dispersant (solid fraction ratio by weight)	60/1	9/1	30/1	27/1	60/1										60/1
Properties	Pigment content (%)	74.8	34.2	60.1	64.5	74.8										74.3
	Particle size ¹⁹ (μ)	5	5	5	5	5										5
	Viscosity (60 rpm) Poise	14.3	9.5	13.8	10.3	11.3										30.0

Table 6

Item	Example	1	2	3	4	5	6	7	8	9	10	11	12
Aqueous Pigment Dispersion	(1)	10	10	10									
	(2)				10								
	(3)					10							
	(4)						10						
	(5)							10					
	(6)								10				
	(7)									10			
	(8)										10		
	(9)											10	
	(10)												10
Aqueous Resin	Aqueous dispersion type	23.4			137.5	65.3	13.7	18.8	23.4	23.4	23.4	23.4	23.4
	cationic emulsion ¹⁰												
Pigment/Resin (solid fraction ratio by weight)	Cationic Emulsion ¹¹		23.4	23.4									
		0.8/1.0	0.8/1.0	0.8/1.0	0.05/1.0	0.2/1.0	1.0/1.0	0.8/1.0	0.8/1.0	0.8/1.0	0.8/1.0	0.8/1.0	0.8/1.0
Paint Film Performance	Film thickness (μ)	35	43	42	34	33	34	37	37	36	36	36	35
	Gloss (60°)	97	93	89	98	97	85	97	73	97	98	99	97
	Chequer board Adhesion Test	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Pass
	Water resistance	No Anomaly	No Anomaly	No Anomaly	No Anomaly	No Anomaly	No Anomaly	No Anomaly	No Anomaly	No Anomaly	No Anomaly	No Anomaly	No Anomaly
	Pencil Hardness	H	B	B	H	H	H	H	H	H	H	H	H

Table 7

Item	Example	13	14	15	16	17	18	19	20	21
Aqueous Pigment Dispersion	(11)	10	10	10						
	(12)				10					
	(33)					10				
	(14)						10			
	(15)							10		
	(16)								10	
	(17)									10
Aqueous Resin	Aqueous dispersion type	23.4			172.0	75.4	107.5	23.3	23.3	23.3
	cationic emulsion ¹⁰									
Pigment/Resin (solid fraction ratio by weight)	Cationic Emulsion ¹¹		23.4	23.4						
		0.8/1.0	0.8/1.0	0.8/1.0	0.05/1.0	0.2/1.0	0.15/1.0	0.8/1.0	0.8/1.0	0.8/1.0
Paint Film Performance	Film thickness (μ)0	36	46	47	35	34	37	35	33	34
	Gloss (60°)	98	93	85	95	94	82	95	97	92
	Chequer board Adhesion Test	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Pass
	Water resistance	No Anomaly	No Anomaly	No Anomaly	No Anomaly	No Anomaly	No Anomaly	No Anomaly	No Anomaly	No Anomaly
	Pencil Hardness	H	HB	F	H	H	H	H	H	H

Table 8

Item	Example	22	23	24	25	26	27	28	29	30	31
Aqueous Pigment Dispersion	(18)	10	10	10							
	(19)				10						
	(20)					10					
	(21)						10				
	(22)							10			
	(23)								10		
	(24)									10	
Aqueous Resin	(25)										10
	Aqueous dispersion type	23.4			170.0	75.0	107.7	23.3	23.3	23.2	23.1
	cationic emulsion ¹⁰										
Pigment/Resin (solid fraction ratio by weight)	Cationic Emulsion ¹¹		23.4	23.4							
		0.8/1.0	0.8/1.0	0.8/1.0	0.05/1.0	0.2/1.0	0.15/1.0	0.8/1.0	0.8/1.0	0.8/1.0	0.8/1.0
Paint Film Performance	Film thickness (μ)	38	46	42	35	35	35	36	34	32	34
	Gloss (60°)	98	92	88	97	96	86	97	94	96	93
	Chequer board Adhesion Test	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Pass
	Water resistance	No Anomaly	No Anomaly	No Anomaly	No Anomaly	No Anomaly	No Anomaly	No Anomaly	No Anomaly	No Anomaly	No Anomaly
	Pencil Hardness	H	HB	B	H	H	H	H	H	H	H

Table 9

Item	Example	32	33	34	35	36	37	38	39	40	41
Aqueous Pigment Dispersion	(26)	10	10	10							
	(27)				10						
	(28)					10					
	(29)						10				
	(30)							10			
	(31)								10		
	(32)									10	
	(33)										10
Aqueous Resin	Aqueous dispersion type cationic emulsion ¹⁰	23.4			171.0	75.1	107.5	23.4	23.3	23.3	23.2
	Cationic Emulsion ¹¹		23.4	23.4							
	Pigment/Resin (solid fraction ratio by weight)	0.8/1.0	0.8/1.0	0.8/1.0	0.05/1.0	0.2/1.0	0.15/1.0	0.8/1.0	0.8/1.0	0.8/1.0	0.8/1.0
Paint Film Performance	Film thickness (μ)	37	45	43	37	36	38	33	35	39	33
	Gloss (60°)	98	91	86	95	99	83	93	94	96	92
	Chequer board Adhesion Test	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Pass
	Water resistance	No Anomaly	No Anomaly	No Anomaly	No Anomaly	No Anomaly	No Anomaly	No Anomaly	No Anomaly	No Anomaly	No Anomaly
	Pencil Hardness	H	B	B	H	H	H	H	H	H	H

(*1): A ϵ -caprolactone modified vinyl monomer, produced by the Daiseru Kagaku Co. (A compound represented by the formula $\text{CH}_2=\text{CCH}_3\text{COO}-\text{C}_2\text{H}_4-\text{O}-(\text{C}(=\text{O})-\text{C}_5\text{H}_{10}-\text{O}-)_3\text{H}$)

(*2): A ϵ -caprolactone modified vinyl monomer, produced by the Daiseru Kagaku Co. (A compound represented by the formula $\text{CH}_2=\text{CCH}_3\text{COO}-\text{C}_2\text{H}_4-\text{O}-(\text{C}(=\text{O})-\text{C}_5\text{H}_{10}-\text{O}-)_5\text{H}$)

(*3): A compound, produced by the Nippon Yushi Co., represented by the formula $\text{CH}_2=\text{CCH}_3\text{COO}-(\text{CH}_2\text{CH}_2-\text{O})_h-\text{H}$ (where h is an integer of value from 7 to 9).

(*4): A compound, produced by the Nippon Yushi Co., represented by the formula $\text{CH}_2=\text{CCH}_3\text{COO}-(\text{CH}_2\text{CHCH}_3-\text{O})_i-\text{H}$ (where i is an integer value of 5 or 6).

(*5): A compound, produced by the Shinnakamura Kagaku Co., represented by the formula $\text{CH}_2=\text{CCOO}-(\text{C}_6\text{H}_5-\text{O})_2-\phi$ (where ϕ represents a benzene ring).

(*6): Monomer (I): A 50% methacryloxyethyltrimethylammonium chloride aqueous solution

Monomer (II): A 50% 2-hydroxy-3-methacryloxypropyltrimethylammonium chloride aqueous solution

Monomer (III): A 50% Acrylamidopropyltrimethylammonium chloride aqueous solution

(*7): Measured in 40% n-butylcellosolve solution

(*8): Titanium White R-5N: Titanium oxide produced by the Sakai Kagaku Co.

Carbon MA: Carbon black produced by the Mitsubishi Kasei Co.

Copper Phthalocyanine 6YK: Produced by the Toyo Ink.

Yellow GKZR-8: Produced by Kikuchi Shikiso.

(*9): Measured in accordance with ASTM D1201-64

(*10): Epon 1002, a cationic resin comprising polyamide resin and phenylmethane diisocyanate blocked material
Amine (mequ/g resin) = 1.10, resin viscosity (60% butylcellosolve solution) Z. Contained 30 wt% n-butylcellosolve. 0.3 equ. neutralised with acetic acid and

water added to provide a dispersion type emulsion of solid fraction 40%.

(*11): Trade name "Sementex-C" (produced by Ohana Sangyo) Cationic styrene/butadiene latex, solid fraction = 30%

Paint Film Hardening Conditions: The paints prepared using the dispersion type emulsion of (*10) were dried for 30 minutes at 180°C and the paints produced using the cationic styrene/butadiene latex of (*11) were dried for 7 days at 20°C (relative humidity 75%).

Paint Film Performance Tests

An aqueous drier ("Deikunate", cobalt metal content 3%) was added to the aqueous paints indicated in Examples 1 to 41 in an amount of 1 part per 100 parts of resin solid fraction and then the paints were painted on a mild steel sheet. After drying for 3 days at 20°C, 75% relative humidity, the samples were subjected to testing.

Chequer Board Adhesion: A hundred squares of width 1 mm were cut and cellophane sticky tape was stuck over the top and then peeled away forcibly in this test.

Water Resistance: The sample was immersed in town water at 20°C for 2 days and the paint surface condition was examined visually.

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